

# Self-assembled fractal hybrid dendrites from water-soluble anionic (thia)calix[4] arenes and Ag<sup>+</sup>

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**Abstract** Novel water-soluble anionic *p*-tert-butylthiacalix[4]arene with propanesulfonate fragments has been synthesized. Alkylation of the lower rim of thiacalix[4]arene in the presence of NaH/THF led to *cone* conformation instead of the expected *1,3-alternate* conformer due to metal template effect. The presence of supramolecular associates at the critical micelle concentration of  $1.65 \cdot 10^{-5}$  M were investigated in aqueous solutions by a combination of different techniques (DLS and conductivity). It was observed that the macrocyclic platform decreases the CMC by tenfold as compared with non-macrocyclic analogs. A simple approach for the design of stable monodisperse Ag-based nanoaggregates (near 95 nm) containing ionic Ag and organic ligand–thiacalix[4]arene sulfo derivative in water has been developed. Self-assembled fractal hybrid nanodendrites consisting of water-soluble anionic

(thia)calix[4]arenes and Ag<sup>+</sup> have been obtained in a single step under mild conditions.

**Keywords** Self-assembly · Dendrite · (Thia)calix[4]arene · Ag-based aggregates · Electron microscopy · Mapping · Stable suspensions

## Introduction

The synthesis of stable, concentrated aqueous dispersions with desired physicochemical properties on the basis of silver nanoparticles (Ag NPs) and various Ag-based aggregates containing ionic or metallic Ag is a necessary step in the preparation of nanostructural materials used in microelectronics, electrochemistry, in the synthesis of pigments for optoelectronic sensors, etc. (Ariga et al. 2012; Ariga et al. 2013; Hussain et al. 2003). Fractal hybrid dendrites are a type of nanostructural materials generally formed by self-assembly under far-from-equilibrium conditions; as such, self-assembly is a natural and spontaneous process (Witten and Sander 1981; Melnikau et al. 2013). The creation of fractal hybrid dendrites offers an opportunity for their application in diverse functions such as in catalysis (Mohanty et al. 2010), optics (Polshettiwar et al. 2009), sensor technology (Wen et al. 2006), and in information storage (Zhou et al. 2007), depending on their specific physical and chemical properties. Besides, Ag-based aggregates are often used to produce various materials with antibacterial properties (Landsdown 2010). Silver ions have a pronounced ability to inactivate viruses like smallpox and influenza A-1 and B. They are active against some enteroviruses,

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